

Critical Potentials and Spectra of Oxygen

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ABSTRACT

The spectra.—The OI and OII line spectra and the band spectra of oxygen in the visible and ultra-violet regions as excited in a low-voltage arc discharge-tube were obtained and the critical potentials for excitation were noted.

Critical potentials.—Ionization of the molecule was found to occur at 16.1 volts. The resonance potential at 9 volts formerly assigned to the atom is also a radiating potential for the molecule. Dissociation of the molecule and simultaneous ionization of one atom occurs at 19.5 volts. From this value and that for ionization of the atom, 13.5, the value of 6 volts is obtained for the dissociation potential of the oxygen molecule. This corresponds to an energy of dissociation of 138,000 calories per gram molecule. Doubly ionized atoms first appear in the discharge at about 50 volts.

Energy-levels for band spectra.—Energy-levels for the electronic states were observed at 16.1, 19.2, and 21 volts. To these we may add the level at 9 volts, as that for the neutral molecule.

This paper deals with experiments with oxygen, from which information has been obtained concerning molecular and atomic critical potentials and their interpretation, as based on the attendant spectra, and is a companion to papers by Duffendack¹ and by Duncan² in which are described researches on hydrogen and nitrogen.

A number of observers have reported values for the radiating, resonance, and ionization potentials of oxygen. Franck and Hertz, Hughes and Dixon, and Bishop found a value of about 9 volts for a potential which has recently been ascribed to radiation.³ Mohler

¹ *Physical Review*, 20, 100, 1922; *Astrophysical Journal*, 60, 122, 1924.

² *Ibid.*, 62, 145, 1925.

³ Hughes, *Bulletin of the National Research Council*, No. 10, 1921.

and Foote¹ found the values 7.9 and 15.5 volts for resonance and ionization potentials, respectively, and Boucher² found 8.0 and 14.0 volts for the same quantities. In a study of the spectral relations in oxygen, Hopfield³ found lines leading to the values 9.11 and 13.56 volts for the potentials of the atom. Recently Mackay⁴ found the value of 12.5 volts for an ionization potential, using a tube in which the electrons were furnished by a photo-electric source. He also found ionization setting in at 16 volts. From experiments made with a positive-ray discharge-tube, H. D. Smyth⁵ concluded that in oxygen molecular ions were produced at about 15.5 volts and doubly and singly charged atomic ions at about 22.5 and 23 volts, respectively.

Apparatus.—The discharge-tube (Fig. 1) used during the spectroscopic investigation was provided with a quartz plate cemented to a side tube. In the other experiments no side tube was used. The cathode consisted of a spiral of 0.25 mm platinum wire wound on an arbor 0.51 mm in diameter. The spiral was heated in concentrated nitric acid, ammonium hydroxide, and distilled water in turn to clean it, and then it was coated with a mixture of barium, calcium, and strontium oxides. The anode was made of a nickel strip bent into the form of a U of such a size as to make the distance from filament to anode about 3 mm. A liquid-air trap was placed near the tube to prevent the access of mercury vapor, and the tube was thoroughly baked out during the exhausting process. The apparatus was evacuated by a mercury-vapor condensation pump. Oxygen was first prepared by the electrolysis of a solution of barium hydroxide and later by heating potassium permanganate in a side tube sealed on the pump system. The gases from the two sources gave identical spectra.

The circuit used was essentially that shown in Figure 1. The anode voltage as read on the voltmeter is that measured from the negative end of the filament. There is a correction to be applied

¹ *Journal of the Optical Society of America*, **4**, 49, 1920.

² *Physical Review*, **19**, 189, 1922.

³ *Astrophysical Journal*, **59**, 114, 1924.

⁴ *Philosophical Magazine*, **46**, 828, 1923; *Physical Review*, **24**, 319, 1924.

⁵ *Proceedings of the Royal Society, A*, **105**, 116, 1924.

because of the voltage-drop along the filament leads and along the filament itself. The middle of the filament is most effective in emission so the correction is made by subtracting one-half of the voltage-drop along the filament and its leads from the reading of the anode

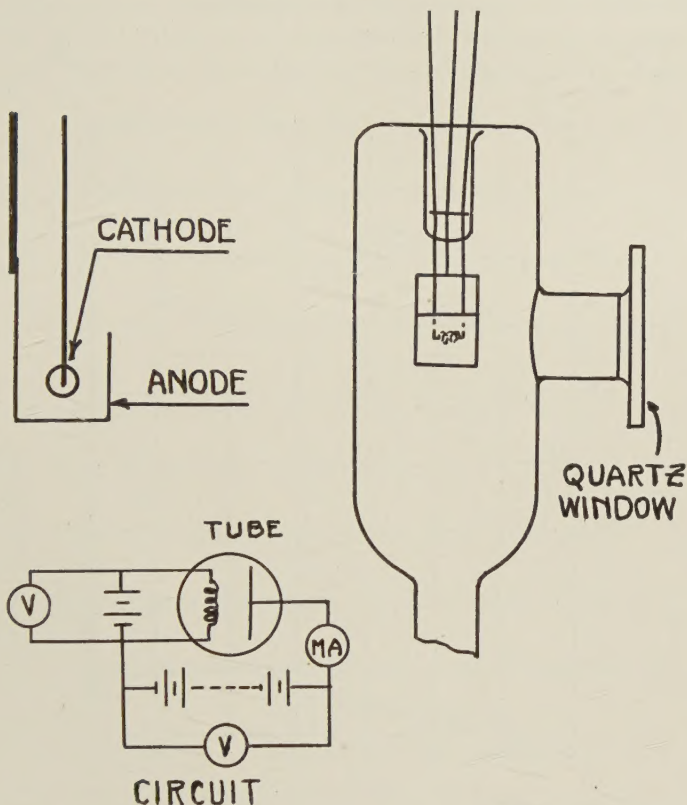


FIG. 1.—Tube, electrodes, and circuit

voltmeter. In discussing the development of spectra this corrected voltage is the one given.

Determination of arcing potential.—Oxide-coated platinum, bare tungsten, and molybdenum filaments were used, most of the work being done with the oxide-coated filaments. Two series of tests were made on the low-voltage arc with a tube of the type described. The conditions of gas pressure and filament temperature influenced the

potential at which the curves broke; therefore one series of tests was made with constant filament temperature and different gas pressures to determine the pressure at which an arc could be maintained at the lowest voltage, and the other was made at the optimum pressure but with varying filament temperature.

In Figure 2 is shown a current-voltage curve for the arc typical of those from which the values for the arcing potentials were ob-

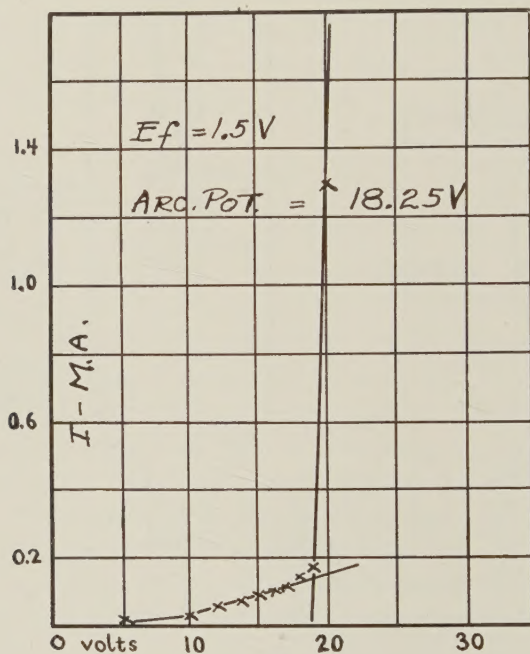


FIG. 2.—Current-voltage curve

tained. All curves showed a distinct break, and the values obtained with decreasing voltage agreed within the limit of error with those obtained with increasing voltage.

The variation in arcing potential with gas pressure is shown in Figure 3a. At low pressures the arcing potential is high. It decreases to a minimum at 0.7 or 0.8 mm, and then it increases with further increase in pressure. At low pressures the mean free path between effective collisions is large compared to the spacing of the

electrodes, and there are not many collisions of electrons with molecules. At the optimum pressure the electrons make the largest number of effective collisions during their travel from cathode to anode. At higher pressures the energy of the electrons is dissipated

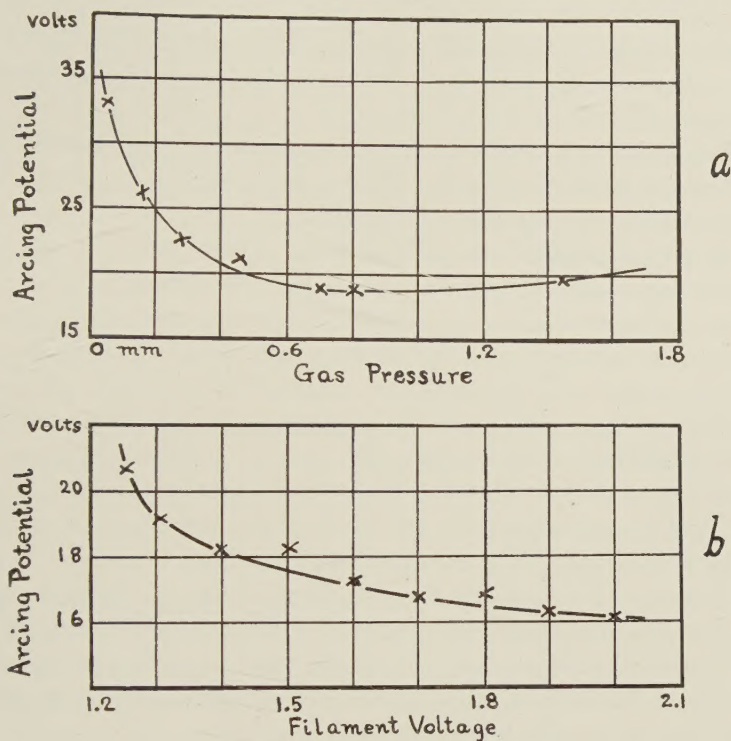


FIG. 3.—Variation in arcing potential:
a, with gas pressure;
b, with filament voltage at optimum pressure.

by inelastic collisions and momentum exchanges with the molecules.

The variation of the arcing potential with the filament temperature at the optimum pressure is shown in Figure 3*b*. The lowest value obtained for the arcing potential was 16.1 volts, corrected for filament drop. The curve shows that a slightly lower value may be obtained for the arcing potential, but that it cannot be far different from that given above. Below this minimum arcing potential of

16.1 volts not enough positive ions are formed to show on the current-voltage curves and accordingly this value is taken to represent the critical potential for an ionization process.

Experiments with filaments of tungsten and molybdenum gave essentially the same results. With tungsten the lowest break came with a corrected voltage of 15.5 volts. The molybdenum filaments had only a very short life but their behavior was similar to that of tungsten.

Spectroscopic studies.—In this part of the investigation the determination of the critical potentials for the excitation of line and band spectra is the important feature.

In determining the value of any one critical potential a number of spectrograms were obtained at small steps of voltage under conditions which gave the largest possible electron current in the tube and the greatest sensitivity of the spectrograph. Since the intensity of any particular radiation increases rapidly after its critical potential has been exceeded, it is possible to obtain a definite value for this quantity. Whenever it was possible, several photographs were examined so as to narrow the limits of the voltages for the appearance and non-appearance of the radiation. Due to the lack of homogeneity in the electron stream because of the initial velocities of the electrons and because of the voltage-drop along the filament, it is not possible to excite one radiation without another if the difference in the critical voltages is small. In one case, however, photographs taken with but 0.3 volt steps did show the progressive extension of a band system, as would be expected.

The "OI" line spectrum.—The low-voltage arc type of excitation favors the band spectra. Relatively few of the lines appear, and these are in the region 6500 to 3600 Å. There may be other lines present which are obscured by the bands. The line 4368 Å, $1S-3P$, of the singlet principal series is the strongest line found in the spectral region studied. The next line of this series, 3692 Å, $1S-4P$, is considerably weaker. No other lines of the singlet series appear with any certainty. The triplet 3947 Å, $1S-3P_{123}$, of the principal series is second in order of intensity. Most of the lines of the triplet sharp and diffuse series have been identified. The lines have intensities corresponding to those given by others, with the exception

of the triplet at 4589 as observed on a 100-volt plate. This line is the last one observed in the series and has an intensity of 10 as compared with an intensity of 2 for the previous line of the same series. In this case it seems probable that there is a line of the enhanced spectrum superimposed on the sharp triplet.

The "OII" line spectrum.—Photographs taken at 45 and 50 volts showed certain lines appearing at the latter voltage which were not present before. These lines have been identified as belonging to the OII or first enhanced spectrum. At 100 volts most of the lines given by Eder and Valenta¹ as being of the spark or OII spectrum of oxygen between 4705 and 4180 Å were observed with about the correct intensity. Two lines not given by Eder and Valenta appeared at 4648 and 4227 with intensities of 10 and 8. This latter line may be confused with the strong calcium line at a slightly shorter wavelength. In this case it is probably due to the excitation of calcium from the filament.

Development of the line spectra.—The first line, 4368 Å, 1S—3P, of the singlet series appears at 16.7 volts, faintly. Then appear the lines at 3947, 6156, 5330, 4968, and 5436, all triplets, in this order. This development is one of intensity, however, and not of energy-levels, for the intensities of the lines are graded, and with longer exposures the lines will appear at lower voltages.

The intensities of both 4368 and 3947 Å increase markedly between 18.8 and 19.8 volts on one plate and between 19.2 and 20.2 volts on another. The explanation of this is as follows: We obtain the atomic lines down to the critical ionization potential 16.1 volts by cumulative action which only occurs with a relatively heavy anode current. In this cumulative process the first collision of an electron with a molecule may dissociate it so that a second electron colliding with one of the atoms is able to ionize it, or atoms may be produced by dissociation in impacts of the second kind with excited molecules and these resulting atoms ionized by a subsequent electron impact. At a higher voltage the electron is able to dissociate the molecule and ionize one of the atoms in a single collision, or ionize the molecule and excite it so that it will dissociate upon collision with a neutral molecule. When this voltage is reached the

¹ *Atlas typischer Spectren*, 85.

atomic ionization will be far more intense because the probability of this kind of process is far greater, and consequently the atomic lines increase in intensity. From the figures given above, we conclude that the value 19.5 volts best represents the voltage at which occur the dissociation and ionization processes as the result of a single electron encounter.

The low intensity of the atomic lines below 19.5 volts gives further credit to the conclusion that the arc is not maintained by atomic ions produced by cumulative action, but rather by molecular ions produced directly. Since the probability of cumulative action is normally slight, the total number of atomic ions produced when there is no arc is very small because the portion of the path of an electron in which effective collisions can occur is short. When there is an arc, most of the drop in potential between anode and cathode occurs near the cathode, the path for an effective collision becomes much larger, and more atomic ions are produced by cumulative action. The first enhanced lines appear at 50 volts, and so we may take this as an approximate figure for the critical potential for the double ionization of the oxygen atom.

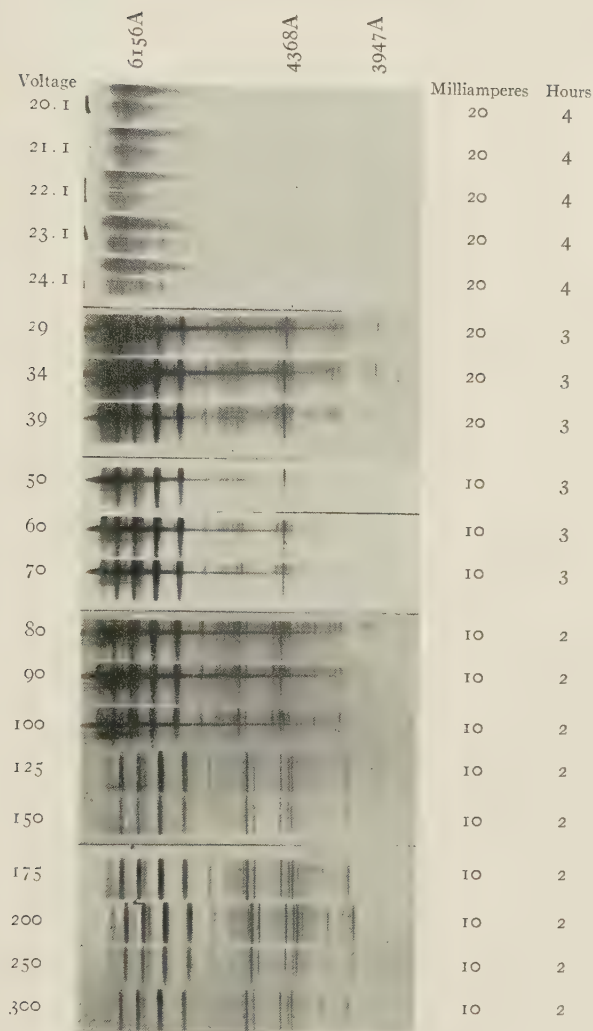
The development of the *OI*, *OII*, and band spectra is shown on Plate XIII for the visible region from 20.1 to 300 volts. The currents and times of exposure of the plates are given. The enhanced lines are first visible at 60 volts. At 300 volts, they are more intense than the *OI* lines and relatively far more intense than the bands.

Excitation at 1000 volts.—A tube was made with an oxide-coated filament of the usual type but with the cathode placed at a distance of 3 cm from the anode. A bulb of about 6-cm diameter was blown in the tube for clearance around the elements.

In one case a discharge was started and maintained in the tube at 700 volts and 5 ma,[†] and gas pressure of about 0.1 mm, without heating the filament by the battery. While the discharge was passing the filament fluoresced, giving off a yellow light. In another case the discharge was self-maintained with 1000 volts, a current of 3.5 ma, and a gas pressure of 0.36 mm. A discharge similar but for a shift in the position of the glow was obtained with the filament

[†] Abbreviation for milliamperes.

PLATE XIII



DEVELOPMENT OF OXYGEN SPECTRA IN THE
VISIBLE REGION

heated. When viewed from a point along the direction of the filament with the filament heated, the glow seemed to consist of two distinct parts separated by a sharp line (see Fig. 4). The glow around the cathode was of a reddish-violet color while the remainder was the yellow-green characteristic of the low-voltage discharge. Ex-

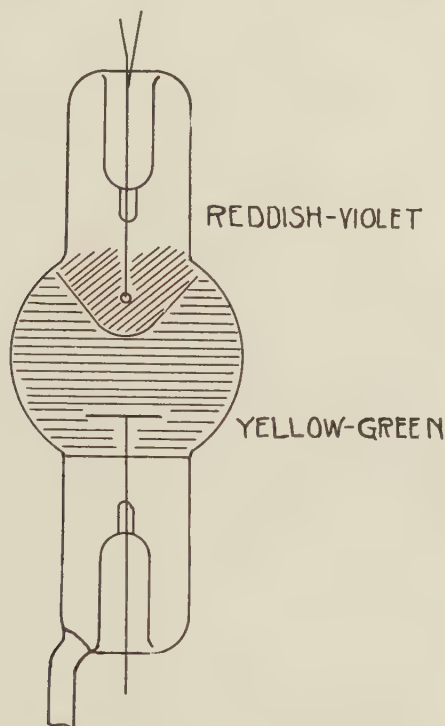


FIG. 4.—Glow at 1000 volts

amination with a spectroscope revealed that most of the light of the cathode glow came from the triplet at 6156 and the OII lines. The green glow came from the negative bands in the red and green.

When the glow was self-sustaining, the space of red glow was larger and less clearly defined than when the filament was heated and the green glow occupied only a small space around the anode. As the gas was "cleaned up," the red glow extended and the green glow faded out. It was necessary to admit gas every 15 or 20 minutes under these conditions.

Photographs showed the OI and OII spectra to be present in both glows. Only a trace of the negative bands was found in the red glow, but in the green glow they were strong. We may conclude from this that in the cathode glow the concentration of molecules is much smaller than in the remainder of the tube.

Energy-levels in the band spectra of oxygen.—The emission of band spectra by molecules is brought about by transitions in state of their electronic, vibrational, and rotational energy from greater to less energy.¹ If details of the spectra are well-enough known it should be possible to construct a complete diagram of the energy-level for the molecular spectra similar to those for atomic spectra.² In no case has the complete diagram been worked out, but for several elements, as oxygen, some of the levels have been evaluated. For oxygen three levels for the electronic state have been determined. The levels of the vibrational state are too close to be found by a study of the critical excitation potentials.

The best known of the emission bands of oxygen are those which comprise what will be called the "second negative band system,"³ extending from red to green at 6853–6567, 6420–6300, 6032–5783, 5633–5540, 5290–5200, and 5005–4955 Å.⁴ These bands give the yellow-green color to the negative glow in a Geissler tube.

Extending from 4870 Å in the visible to about 2200 Å and perhaps beyond are other bands which will be designated as belonging to the "first negative system." Johnson⁴ has photographed these bands in a Geissler-tube discharge and has given an analysis of the system.⁵ The wave-lengths of these bands as noted by the writer agreed with those given by Johnson. The appearance of the first negative bands under the experimental conditions obtaining here

¹ Sommerfeld, *Atombau und Spektrallinien*, chap. vii.

² Duffendack, *Astrophysical Journal*, **61**, 209, 1925.

³ The names "first" and "second" negative band systems were assigned to these particular bands because they appear in the order given, as the voltage of the tube is increased, and they both belong to the ionized molecule, as will be shown. The term "negative bands" has been generally applied to those which are more intense in the negative glow of a Geissler-tube discharge than in the positive column. The term "positive bands" is applied to those which are more intense in the positive column.

⁴ R. C. Johnson, *Proceedings of the Royal Society of London*, A, **105**, 683, 1924.

⁵ Professor Birge, of the University of California, states in a letter that he has assigned new quantum numbers, n' and n'' , to these bands by making the substitutions, $n' = 33 - n$, and $n'' = 55 - p$, n and p being the quantum numbers of Johnson.

confirms his conclusion that these bands are not due to ozone. In the experiments any ozone would have been taken up immediately by the liquid air and the gas would have been "cleaned up" rapidly. No such clean-up was noted until at about 70 volts, and the bands appeared first at 19.2 volts.

The so-called "water-vapor" band¹ at 3064 Å appeared alone on some plates taken at about 18 volts. This band has been studied by several others, who have concluded that it is due to an *OH* molecule.² In the work of the writer the use of liquid air on the vacuum system eliminated the possibility of the presence of a large amount of water vapor. It is possible that a small amount could have been produced by vapors from the cement used in sealing on the quartz plate. This, of course, would not have been taken up by the liquid air until it had diffused to the trap.

The first negative bands appear on one set of plates at about 19.2 volts. At 18.2 volts, only the water-vapor band and the line 4368 are visible. At 19.2 volts, the band heads at 4352-4314, 4116-4063, 3958-3962, and 3734-3705 Å appear faintly. At 20.2 volts, the bands are developed to about 2300 Å. Since the first negative bands appear earliest at 19.2 volts, this value is taken to represent an energy-level for the initial electronic state of these bands. There is no trace of the second negative bands on one plate at 20.1 volts, but they are quite plain at 21.1 volts. On another plate the bands are visible at 21.8 volts, but not at 20.8. We may thus take 21 volts as the critical value for these bands. No changes in the bands occur at the highest voltages, but they become relatively weaker than the lines, due to an increase in the percentage of dissociation, and, of course, the enhanced lines appear on the plates.

We have just obtained two energy-levels for electronic states of the molecule. The vibrational levels for each state will be in steps slightly above the corresponding electronic levels, and those for the rotational states will be grouped around the vibrational levels. Only the electronic levels, however, will be considered. If a molecule in the 21-volt state reverts to the 19.2-volt state with the emission

¹ Steubing, *Annalen der Physik*, **33**, 553, 1910.

² Watson, *Physical Review*, **23**, 768, 1924. Dr. Barker, of the University of Michigan, also arrived at the same conclusion.

of radiation, the energy emitted will be that corresponding to the potential difference 1.8 volts, and the wave-length will be about 6850 Å, as given by the equation $\lambda = hc/Ve$. One of the second negative bands emitted during such a transition of the molecule has been observed at 6853–6567.

We will now consider the process of finding the final energy-level of the first negative bands from the initial level and the wave-length of the radiation. The earliest of the first negative bands to appear toward the violet is the one at 3734–3705. The voltage difference between the initial and final states calculated from the wave-length is about 3.3 volts, and the final level is thus 15.9 volts. In the experiments discussed in the first part of the paper an ionization potential was found at 16.1 volts. Since an accuracy to a tenth of a volt is beyond realization in this type of measurements, the agreement is rather good. Because of this agreement, we now interpret the ionization potential of 16.1 volts, previously obtained, as being an energy-level for the molecule, and in particular the lowest level for the ionized molecule. Photographs taken at voltages below 16.1 volts with tubes of two and of three elements showed no bands or lines in the region studied. All radiation produced at voltages below this value must be in other spectral regions.

It is interesting to note that only every other one of the bands found by Runge and Grotrian¹ were seen by Johnson and the writer, the others being missing. The ones found were those at 2983, 3233, 3516, 3841 Å, and the missing ones were those at 3104, 3370, and 3673 Å. It is possible that the high voltage and higher pressure excitation of Runge and Grotrian favored the development of these particular bands.

Interpretation of critical potentials.—Three energy-levels for the band spectra 21, 19.2, and 16.1 volts, have been found. This last potential has been interpreted as the ionization potential for the oxygen molecule. The value of 19.5 volts has been obtained for the potential at which dissociation of the molecule and ionization of an atom occur as the result of a single electronic encounter. A potential of 50 volts is sufficient for the production of doubly ionized oxygen atoms. My value for the ionization potential is in agreement with

¹ *Physica*, 1, 254, 1921.

that of Mohler and Foote, the higher value of Mackay, and that of Smyth. Since we have reason to believe that the probability of dissociation of the molecule is very small below 19.5 volts, it will be necessary to interpret the experimentally determined critical potential at 8 or 9 volts as one for molecular radiation as well as for atomic radiation. We may then take this as an energy-level for the molecule.

The difference in the potentials for dissociation and ionization (19.5 volts) and for ionization of the atom (13.56 volts) gives a value of approximately 6 volts for the dissociation potential of the oxygen atom. The energy of dissociation calculated from this value is 138,000 calories per gram molecule.¹

In closing the author wishes to acknowledge his indebtedness to Dr. O. S. Duffendack, of the University of Michigan, for his interest in the work and for the helpful suggestions regarding it.

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¹ See also Wulf, *Journal of the American Chemical Society*, **47**, 1945, 1925.

